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⑤④ **Hydrophilic modifier monomers.**

⑤⑦ Hydrophilic modifier monomers of the formula $(X-div)_zHy$ are disclosed wherein X is a reactive group, Hy is a hydrophilic group and div is a divalent linking group, z being a number up to the available valence of Hy, excess Hy valences being taken up by hydrogen. The monomers of the invention can be used to boost the hydrophilic nature of a wide variety of polymeric materials or be polymerized themselves with varying degrees of copolymerizable monomers. They are particularly suited for making hydrophilic contact lens materials.

EP 0 331 633 A2

Description

HYDROPHILIC MODIFIER MONOMERS

The invention relates to hydrophilic monomers and to their use for modification of oligomers, particularly oligomers used in the manufacture of contact lenses, to increase hydrophilicity of resulting polymers and increase mold compatibility in the manufacture of such molded polymers.

There is an extensive body of literature on hydrophilic monomers in the art and a large number of such monomers is commercially available. These monomers impart hydrophilicity, water absorption, and/or improve the wetting properties of materials having them copolymerized therein over the same material absent such monomers. They also result in highly hydrophilic, highly absorbent, and highly wettable homopolymeric materials. These commercial monomers can be obtained from typical monomeric suppliers such as ROHM Tech, typically under the MHOROMER[®]D series; Sartomer; and Alcolac, typically under the SIPOMER[®] series.

A general characteristic of such known modifiers is that there is a hydrophilic group and a copolymerizable group. A typical example is N-vinyl pyrrolidone; another is hydroxyethylmethacrylate. Each of these is suitable for copolymerizing with other monomers or oligomers containing one or more free (meth)acrylic or vinylic groups. The addition of the free hydroxy or the amide increases the hydrophilicity, water absorbability and wettability of the resulting polymers over those not having such monomers present.

For many utilities, it is desired that the polymeric materials resulting therefrom be in molded form. This is typical in the field of contact lenses. Also frequently, molds are poly(methyl methacrylate) and copolymerizing a) the aforementioned modifying monomers with b) the monomers or oligomers being modified in such molds results in etching and scarring of the molds. This is extremely disadvantageous for ultimate polymer utilities which require mar free surfaces, i.e. high quality optical surfaces. In these situations, molds must be replaced extremely frequently resulting in high production costs and slowed production rates.

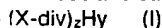
It is therefore an object of the invention to remedy the above defects and provide a hydrophilic monomer which will substantially reduce the amount of mold etching in preparing hydrophilically modified material.

Another object of the invention is to provide hydrophilically modified polymers.

Another object of the invention is to provide contact lenses having increased wettability and/or water absorption.

A still further object of the invention is to provide a contact lens which is surface modified by a hydrophilic modifier monomer.

These and other objects can be realized by utilizing hydrophilic modifier monomers of the formula I,

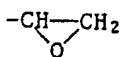


wherein Hy is a hydrophilic portion; div is a divalent linking group; X is a group co-reactive or copolymerizable with other monomers, and z is an integer of 1 up to the valence of Hy and where z is less than the valence of Hy, the remaining valences of Hy are taken up with hydrogens.

The hydrophilic group Hy typically has one or more, preferably a plurality of, free or etherified hydroxy groups, amino groups, amido groups, urethane groups, and/or other typically hydrophilic groups. div is generally a divalent linking group which can be selected from a wide variety of divalent groups. The only general limit on div is that it can be linked to both Hy and X.

More specifically, X is a polymerizable or reactive moiety selected from

- a) ethylenically unsaturated radicals, preferably vinyl, 1- or 2-lower alkyl vinyl, more preferably 1-methyl vinyl, or 2-methyl vinyl, or allyl;
- b) epoxy groups such as

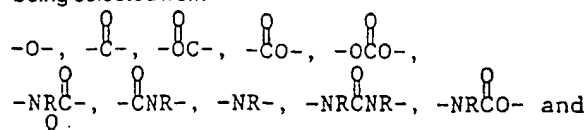


and glycidyl;

- c) radicals of anhydrides such as of maleic anhydride, phthalic anhydride, or acetic anhydride;
- d) isocyanato;
- e) isothiocyanato;
- f) amino groups;
- g) acyl groups, particularly carboxyl;
- h) ester groups, especially of alcohols or acids that are readily displaceable;
- i) amido groups;
- j) carbamoyl groups;
- k) acid halide groups, especially carbonyl chloride;
- l) ether groups; and
- m) hydroxy; div is selected from

aa) a divalent aliphatic group of up to 25 carbon atoms, preferably an alkyl, an alkenyl, or an alkynyl group, preferably of up to 20 carbon atoms, more preferably of up to 15 carbon atoms, still more

preferably of up to 10 carbon atoms, and most preferably of up to 5 carbon atoms, and preferably of at least 2 carbon atoms, more preferably of at least 4 carbon atoms, which aliphatic group may be interrupted, or terminated, or interrupted and terminated by an interrupting and/or a terminal group each being selected from



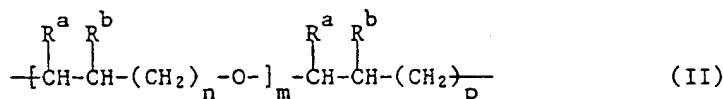
in which R is hydrogen, or lower alkyl, e.g. C₁₋₄ alkyl;

ab) a divalent 5-7 membered cycloaliphatic ring and a divalent (5-7 membered cycloaliphatic)-C₁₋₂₀ aliphatic group, in which the non-cyclic portion is preferably alkyl, alkenyl, or alkynyl and preferably has up to 15 carbon atoms, more preferably up to 10 carbon atoms, most preferably up to 5 carbons, and preferably has at least 2 carbon atoms, more preferably has at least 4 carbon atoms, and the non cyclic portion may be interrupted, or terminated, or interrupted and terminated by an interrupting and/or terminal group selected from those set forth in aa) above;

ac) a divalent arylene group having 6-25 carbon atoms, preferably 6-18 carbon atoms, more preferably 6-10 carbon atoms, most preferably 6 carbon atoms, which is unterminated or terminated by a terminal group selected from those set forth in aa) above;

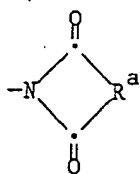
ad) a divalent-(aliphatic)_a-aryl-(aliphatic)_b-group of 8 to 25 carbon atoms, wherein one of a and b is 1 and the other is zero, or both a and b are one, and each aliphatic portion is independently selected from the same aliphatic groups set forth in aa) above and may be interrupted, or terminated, or interrupted and terminated as indicated in aa) above; and

ae) a group of the formula II



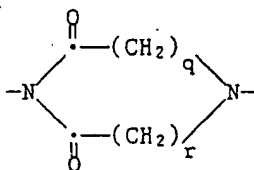
wherein m is 8-100; and aea) R^a is hydrogen, R^b is methyl, and n and p are each zero; aeb) R^a is methyl, R^b is hydrogen, and n and p are each zero; or aec) R^a and R^b are each hydrogen and n and p are each 1; and each group within aa) to ad) is unsubstituted or substituted by at least one substituent selected from halogen, C₁₋₄ alkyl, and perhalo C₁₋₁₂ alkyl; and Hy is a hydrophilic group selected from

i) morpholino; cyclic mono amide radicals of 5-7 ring members which are selected from carbon and one nitrogen; saturated and unsaturated cyclic radicals having 5-6 ring members of the formula III,



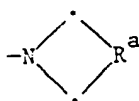
(III)

wherein R^a is alkylene or alkenylene of 2 or 3 carbons, cyclic amides having 6-7 ring members of the formula IV,



(IV)

wherein g and r are each independently 0-2, and cyclic amines of the formula

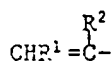


(V)

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- 10 wherein R^a is alkylene or alkenylene of 2 or 3 carbons;
 each of which is unsubstituted or substituted by hydroxy -C₁₋₅ alkyl, carboxy, or lower alkyl;
 ii) tetrahydrofurfuryl
 iii) mono, di and poly saccharide radicals, whether straight chain or cyclic, having up to 12 carbon atoms
 15 per saccharide unit, their corresponding sugar alcohol radicals, pentaerythritol radicals, and polyvinyl
 alcohol radicals; and
 iv) polyhydroxy C₂₋₇ alkyl radicals.
 Preferably, X is a vinylic group selected from formula VI

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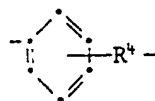


(VI)

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and the portion of div bound thereto terminates in -C(O)R³- of which the carbonyl is bound to X or in

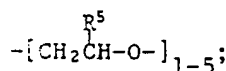
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in which the left hand bond is bound to X; wherein either, in case that each of R¹ and R² is hydrogen or methyl,
 R³ is selected from -O- or -NR⁵- provided that the next atom of div to which it is bound is other than oxygen or
 nitrogen, or R³ is a bond provided that the next atom of div to which it is bound is other than a carbonyl carbon,
 and R⁵ is hydrogen or lower alkyl; or
 in case that R¹ is hydrogen or methyl, and R² is hydrogen, lower alkyl or cyano, R³ is lower alkylene or

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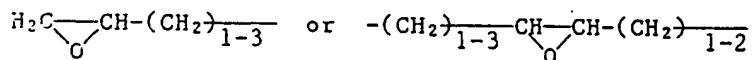


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and in each case R⁴ is -O-, -C(O)-, -OC(O)-, -C(O)O-, -NR⁵C(O)-, -OC(O)O-, -NR⁵-, -NR⁵C(O)O-, -C(O)NR⁵,
 -OC(O)NR⁵-, or -NR⁵C(O)NR⁵ provided that the next atom of div to which it is attached is other than oxygen or
 nitrogen;

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or X is an epoxy group of the formulae

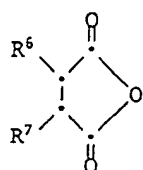


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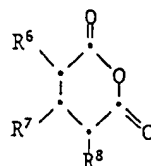
or X is an anhydride residue of the formulae VIII or IX,

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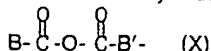
(VIII)



(IX)

wherein at least one of R⁶ and R⁷ in formula VIII and at least one of R⁶-R⁸ in formula IX is a bond, the others being a bond, hydrogen, lower alkyl or two adjacent groups R⁶-R⁸ in formula IX together with the atoms to which they are attached form a C₅₋₈ cycloalkyl or cycloalkenyl ring or form a benzene or naphthalene ring; and the unsaturated analogs thereof;

or X is an anhydride residue of the formula X,

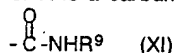


wherein B is C₁-C₆ alkyl, C₂-C₆ alkenyl or phenyl or naphthyl or has the meaning of B', and B' is C₁-C₆ alkylene, C₂-C₆ alkenylene or phenylene or naphthylene;

or X is isocyanato, isothiocyanato, amino, or -NH(loweralkyl);

or X is an acyl, preferably carboxyl, or is an acyl halide, preferably an acyl chloride, or is an acyl ester, preferably of a lower alkyl alcohol, more preferably of a primary alcohol, or an amide, preferably of a lower alkyl amine, more preferably of a lower alkyl primary amine;

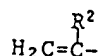
or X is a carbamoyl of the formula XI



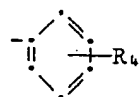
wherein R⁹ is amino lower alkyl;

or X is an ether group of the formula -O-R¹⁰ wherein R¹⁰ is lower alkyl or is a cyclic ether residue having a total of 4 to 7 ring members only one of which is oxygen, the remaining ring members being carbon, the bond to div being other than the alpha and omega carbons of the ring when it is bound to an oxygen atom of div; or X is hydroxy;

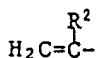
Further preferred X groups are 1-methylvinyl, 2-methylvinyl, or allyl; or



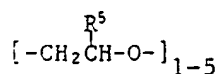
wherein R² is hydrogen or methyl and the portion of div to which it is attached terminates in -C(O)-R³- with the carbonyl being bound to X, and R³ is -O- or -NR⁵- with R⁵ being hydrogen or lower alkyl; or H₂C=CH- and the portion of div to which it is attached terminates in



the left hand bond being bound to X, wherein R⁴ is -O-, -NR⁵-, -C(O)-, -C(O)NR⁵-, or -C(O)O-; or



wherein R² is hydrogen, lower alkyl, or cyano and the portion of div to which it is attached terminates in -C(O)-R³-, the carbonyl thereof being bound to X and R³ being lower alkylene or



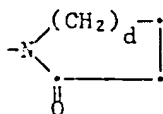
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and R⁵ being lower alkyl.

Preferably Hy is selected from

- 10 ba) morpholino which is unsubstituted or mono- up to tetra-substituted by lower alkyl, preferably methyl or ethyl;
 bb) an amide of the formula XII

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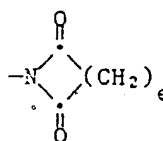
(XII)

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wherein d is 1-3, preferably 1; each of which is unsubstituted or substituted, preferably mono or di substituted, by lower alkyl, preferably methyl or ethyl;

bc) a group of formula XIII,

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(XIII)

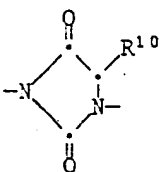
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wherein e is 2-3, preferably 2, each of which is unsubstituted or substituted by lower alkyl, preferably methyl or ethyl;

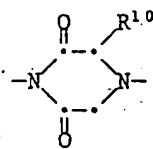
bd) a divalent group of one of the formulae XIV, XV, XVa, XVI, XVIIa or XVIIb,

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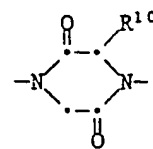


(XIV)

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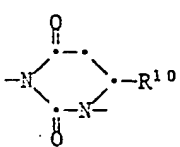


(XV)



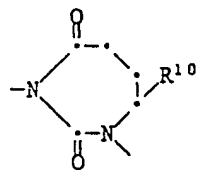
(XVa)

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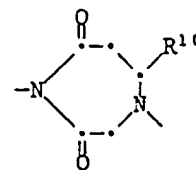


(XVI)

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(XVIIa)



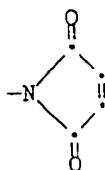
(XVIIb)

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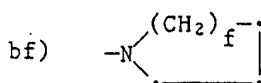
wherein R¹⁰ is hydrogen or carboxy;

be)

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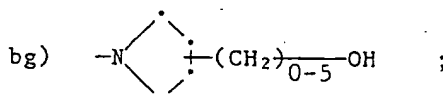
(XVIII)

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wherein f is one or two, each of which is unsubstituted or substituted by lower alkyl, preferably methyl or ethyl;

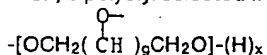
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bh) a polyolyl selected from bha) polyvinyl alcohol radicals, bhb) groups of the formula



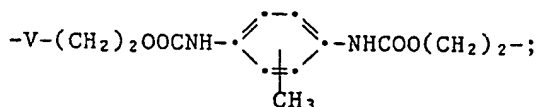
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wherein g is 2-10 and x is an integer from 0.5 g up to g + 1 inclusive; cyclic saccharide analogs thereof; di-tetra saccharides thereof, preferably having saccharide-saccharide links between the 1 and 4 carbon positions, preferably β links; bhc) $\text{C}(\text{CH}_2\text{O}-)_4(\text{H})_i$ wherein i is 0-3; and bhd) polyhydroxy lower alkylene, preferably C_{2-3} alkylene, glycol radicals; wherein in bha) and bhd) above, at least one and up to 50 %, preferably up to 25 %, more preferably 10 %, of the hydroxy groups are missing their alcoholic hydrogens.

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Preferably div is selected from
 $-\text{V}-(\text{CH}_2)_2\text{NHCOO}(\text{CH}_2)_2-$;

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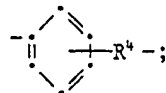


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$-\text{V}-(\text{CH}_2)_2\text{NHCO}-$; and

$-\text{V}-(\text{CH}_2)_2\text{NHCO}(\text{CH}_2)_2-$ in which V is selected from a bond, $-\text{C}(\text{O})\text{R}^3-$, or

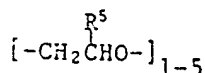
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in each case the left hand bond of V being bound to X; and wherein R^3 is $-\text{O}-$, $-\text{NR}^5-$ or

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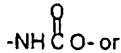
or a bond; R⁵ is hydrogen or lower alkyl; and R⁴ is a bond, -O-, -C(O)-, -OC(O)-, -OOC-, -OC(O)O-, -NR⁵-, -NR⁵C(O)-, -C(O)NR⁵-, -NR⁵COO-, -OOCNR⁵-, or -NR⁵C(O)NR⁵-.

More preferably, X is an ethylenically unsaturated group, i.e. vinyl, 1-lower alkyl vinyl, 2-lower alkyl vinyl, 1,2-di(lower alkyl)vinyl or vinyl-lower alkyl, most preferably vinyl, 1-methyl vinyl, or allyl.

Hy is most preferably pyrrolid-5-one-1-yl, morpholin-1-yl, glycidyl,

(-OCH₂-[CH]₃₋₆-CH₂O-)H₄₋₇ radicals, (HOCH₂)₃C-, [HOCH₂]₃C-CH₂O-, or a polyvinylalcohol radical. div is most preferably an alkyl of 2-6 carbons which is terminated on one side by carbonyloxy,

ca) the carbonyl being bound to X and being interrupted once by



cb) terminated at the other side by

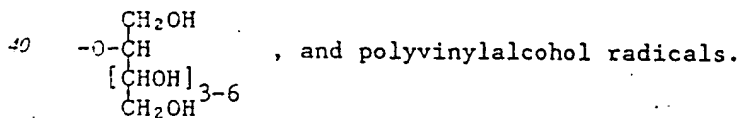
-NH-C(=O)-, the carbonyl being bound to Hy, preferably the carbonyl being bound to an oxygen atom of Hy. The alkyl of div is most preferably of 2 or 4 carbon atoms.

A second most preferably group div is a divalent -C(O)O-aliphatic-OC(O)NH-aryl-NHC(O)O-aliphatic-group with the terminal carbonyl group being bound to X. In such groups the aryl is preferably a phenyl or naphthyl, unsubstituted or substituted by halogen or C₁₋₄ alkyl, most preferably substituted by methyl. In such groups, each of the aliphatic groups is preferably an alkyl of up to 10 carbon atoms, more preferably up to 5 carbon atoms. Most preferably such aliphatic groups are -CH₂CH₂-.

Most preferred are the monomers of formula I wherein X is vinyl or 1-methyl vinyl; z is one; div is selected from -C(O)O-C₂₋₆-alkyl- which is interrupted once by -NHC(O)O- within the alkyl portion, the terminal carbonyl group being bound to X; the same group as defined directly hereinbefore terminated on the alkyl side by 1 to 19 additional oxyalkylene groups;

-C(O)O-C₂₋₆-alkyl-NHCO-, the terminal carbonyl group of the oxycarbonyl portion being bound to X; -aryl-NHCO-, the aryl-portion of which is bound to X; -aryl-NHC(O)O-C₂₋₄-alkyl-, the aryl-portion of which is bound to X; and -C(O)O-C₂₋₆-alkyl- which is interrupted once by -OCONH-aryl-NHCOO- in the alkyl portion, the terminal carbonyl group of which is bound to X; wherein aryl is phenyl or phenyl substituted by C₁₋₄-alkyl, preferably methyl;

and Hy is selected from pyrrolidin-5-one-1-yl, morpholin-1-yl, glycidyl, -C(CH₂OH)₃.



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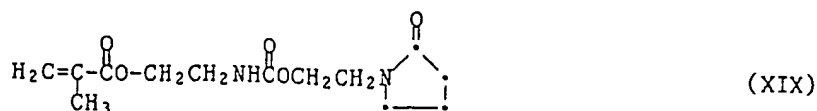
The most highly preferred monomers of the invention are of formula XIX to XXIV,

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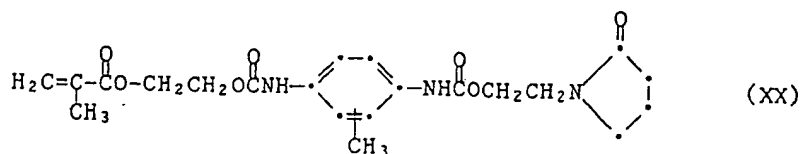
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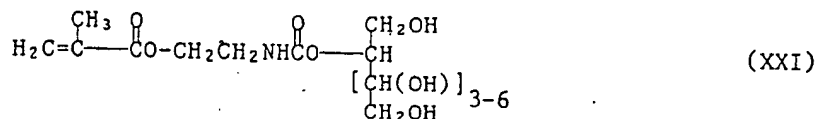
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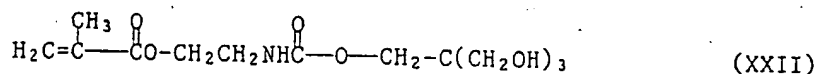
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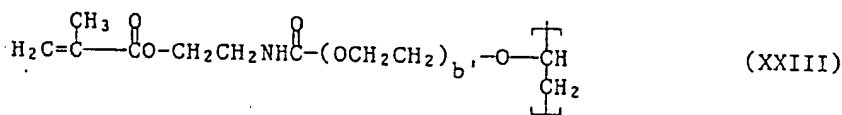
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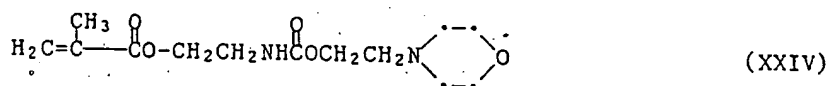


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where b' is the number of repeating units in a typical polyethyleneglycol, especially on average 1 to 20, and formula XXIII represents a portion of a modified polyvinylalcohol macromer; and

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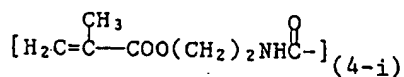


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and the compounds disclosed in the examples. Of these, the monomers of formulae XIX-XXII and XXIV are especially preferred, and most especially those of formulae XIX, XX and XXIV.

Even preferred are the compounds of formula I which are selected from

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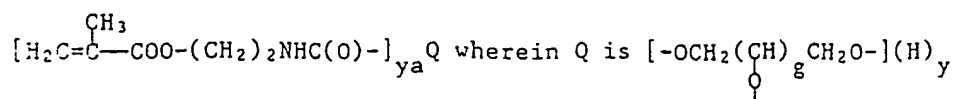


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wherein P is $\text{C}(\text{CH}_2\text{O})_4\text{H}$; and i is 0-3; or P is a polyvinyl alcohol having at least one and up to 50 % of the alcoholic hydrogens thereof absent; and

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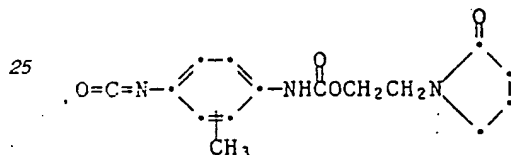
in which g is 1-6 and y is zero up to g+1 and y_a is (g+2-y).

10 The hydrophilic modifying monomers of the invention can be made in a number of ways, the individual steps of which are known in the art. The starting materials are all well known to those in the art and most are commercially available.

One set of starting materials is X-E, W-L-Y, and G-Hy wherein E is coreactive with W, and Y is coreactive with G. When the reactions of E with W and Y with G are complete, the group -EW-L-YG- is div-. The group -L- can be a simple aliphatic hydrocarbon chain without any substituents or interruptions or terminating groups. Alternatively, it can be a complex group having a number of interrupting and/or terminating groups as well as substituents.

For example, toluene diisocyanate can represent a simple W-L-Y compound. Reaction of 1 mole thereof with 1 mole of N-hydroxyethyl pyrrolidone (an G-Hy compound) yields a compound of the formula

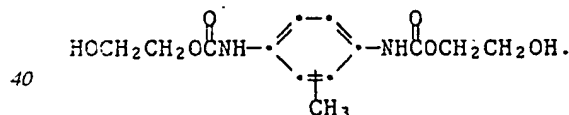
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This can then be reacted with 1 mole of 2-hydroxyethylmethacrylate (an X-E compound) to yield the compound of formula XX. More complex similar structures can be prepared by reacting 1 mole of toluene diisocyanate with 2 moles of ethylene glycol to yield a compound of the formula

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45 Depending on the final desired compound, one mole of this can be reacted with a) 1 mole of an isocyanato-Hy type compound, such as N-(2-isocyanatoethyl)pyrrolidone, and then 1 mole of an isocyanato methacrylate to yield a monomer of the invention or b) 2 moles of a diisocyanato compound which can then be reacted with N-(2-hydroxyethyl)pyrrolidone and 2-hydroxyethylmethacrylate (HEMA) to yield a compound similar to that of formula XX but having 4 interrupting groups and one terminating group.

50 The sequence of reactions can, of course be reversed so that the X-E compound and the W-L-Y compound are first reacted and then a G-Hy compound is reacted with the result. Of course, when G is not reactive with E or X and E is not reactive with G or Hy all three components can be added together simultaneously.

The compound of formula XIX can likewise be prepared from isocyanatoethylmethacrylate (IEM) and 2-hydroxyethyl pyrrolidone. Similarly, compounds of formulae XXI-XXIII can be prepared from IEM and hydroxy containing compounds, i.e. a $\text{HOCH}_2[\text{CH}(\text{OH})]_4\text{CH}_2\text{OH}$ for formula XXI, $\text{C}(\text{CH}_2\text{OH})_4$ for formula XXII, and ethoxylated poly vinyl alcohol for formula XXIII.

55 As one of ordinary skill can appreciate, replacing the above vinyl group part of the IEM) with an appropriate X group yields any of the desired X terminated compounds. Similarly, replacing the N-(2-hydroxyethyl)-pyrrolidone with a N-(2-hydroxyethyl)morpholine yields the product shown in formula XXIV. Synthetic routes to the rest of the monomers within the invention are within the ability of one of ordinary skill in this art.

60 Based on foregoing, the following examples are presented to illustrate, but not limit the invention.

Example 1:

65 To 25.0 g of ethoxylated PVA (which has been previously dried in a vacuum desiccator using P_2O_5) is added 150 g of dry dimethylsulfoxide (DMSO) and 0.004 % stannous octoate. The mixture is stirred for 90 minutes to

ensure that complete solubilization is achieved. To this is added 1 % by weight styrene isocyanate (0.26 g, 0.0017 mol). The reactions completeness is monitored by the disappearance of the isocyanate peak by FT IR. The solution can be used as a hydrophilic modifier as is.

Example 2:

The procedure of example 1 is followed; however 0.0017 mole of isocyanatoethylmethacrylate is used in place of the styrene isocyanate.

Example 3:

To 25.0 g of PVA (Average M.W. = 16,000, 98 % hydrolyzed, which has been previously dried in a vacuum desiccator using P_2O_5) is added 150 g of dry DMSO and 0.004 % stannous octoate. The mixture is stirred for 90 minutes to ensure that complete solubilization is achieved. To this is added 0.5 % by weight styrene isocyanate (0.126 g, 0.0017 mol). The reactions completeness is monitored by the disappearance of the isocyanate peak by FT IR.

Example 4:

The procedure of example 3 is followed; however 0.0017 mole of isocyanatoethylmethacrylate is used in place of styrene isocyanate.

Example 5:

To 25.0 g of PVA (Average M.W. = 86,000, 88 % hydrolyzed, which has been previously dried in a vacuum desiccator using P_2O_5) is added 150 g of dry DMSO and 0.004 % stannous octoate. The mixture is stirred for 90 minutes to ensure that complete solubilization is achieved. To this is added 0.5 % by weight styrene isocyanate (0.135 g, 0.0008 mol). The reactions completeness is monitored by the disappearance of the isocyanate peak by FT IR.

Example 6:

The procedure of example 5 is followed using 0.00085 mole of isocyanato ethyl methacrylate instead of styrene isocyanate.

Example 7:

One mole of glycidol is introduced into a flask and to it is added 0.74 g (0.013 mol) potassium hydroxide. The mixture is placed into a constant temperature bath overnight at 23-27°C. To the mixture is added methanol which is then neutralized with Amberlite IR-120-H resin. The solution is then filtered and the methanol is removed. The material is now dried in a vacuum desiccator for 2 days to ensure that it is dry. The material is then introduced into DMSO and reacted with styrene isocyanate (0.37 g, 0.0026 mol). The completion of the reaction can be monitored by the disappearance of the isocyanate peak.

Example 8:

To a clean, dry 100 ml round bottom flask equipped with condenser, nitrogen inlet and thermometer are added 15.53 g, 0.10 moles isocyanatoethyl methacrylate, 0.02 g dibutyl tin dilaurate and 50 ml methylene chloride. The mixture is stirred under a nitrogen atmosphere to effect solution. To the solution is added 12.93 g, 0.10 moles hydroxyethyl pyrrolidone. After 1.5 hours the isocyanate band is not observed in the FT infrared spectrum. The solvent is removed via stirring under a dry-air purge.

Example 9:

The above modifiers of Examples 1-8 are added to

- a) styrene isocyanate endcapped polypropylene glycol 4000,
- b) the monomers of formula V of US Patent 4,780,488, filed June 5, 1987, or
- c) the monomers of formula I of US Patent 4,740,533, filed July 28, 1987 in amounts of 10 % or 15 % by weight and cured. The resulting polymers all have increased water content over the corresponding polymer without the compounds of examples 1-8 present.

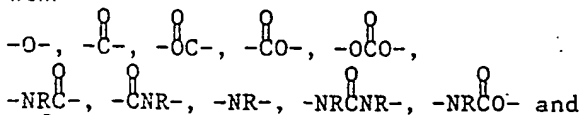
Claims

1. A compound of the formula I,
 $(X-div)_2Hy$ (I)
 wherein X is a polymerizable or reactive moiety selected from
 - a) ethylenically unsaturated radicals;
 - b) epoxy groups;
 - c) radicals of anhydrides;
 - d) isocyanato;
 - e) isothiocyanato;
 - f) amino groups;

g) acyl groups;
 h) ester groups;
 i) amido groups;
 j) carbamoyl groups;
 k) acid halide groups;
 l) ether groups; and
 m) hydroxy;

div is selected from

aa) a divalent aliphatic group of up to 25 carbon atoms, which aliphatic group may be interrupted, or terminated, or interrupted and terminated by an interrupting and/or a terminal group each being selected from



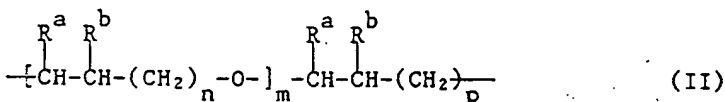
-O-C-NR- in which R is hydrogen, or lower alkyl;

ab) a divalent 5-7 membered cycloaliphatic ring and a divalent (5-7 membered cycloaliphatic)-C₁₋₂₀ aliphatic group, and the non cyclic portion may be interrupted, or terminated, or interrupted and terminated by an interrupting and/or terminal group selected from those set forth in aa) above;

ac) a divalent arylene group having 6-25 carbon atoms, which is unterminated or terminated by a terminal group selected from those set forth in aa) above;

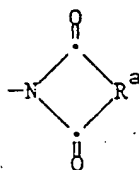
ad) a divalent-(aliphatic)_a-aryl-(aliphatic)_b- group of 8 to 25 carbon atoms, wherein one of a and b is 1 and the other is zero, or both a and b are one, and each aliphatic portion is independently selected from the same aliphatic groups set forth in aa) above and may be interrupted, or terminated, or interrupted and terminated as indicated in aa) above; and

ae) a group of the formula II



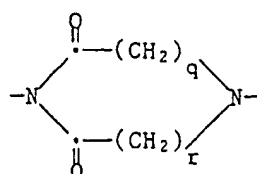
wherein m is 8-100; and aea) R^a is hydrogen, R^b is methyl, and n and p are each zero; aeb) R^a is methyl, R^b is hydrogen, and n and p are each zero; or aec) R^a and R^b are each hydrogen and n and p are each 1; and each group within aa) to ad) is unsubstituted or substituted by at least one substituent selected from halogen, C₁₋₄ alkyl, and perhalo C₁₋₁₂ alkyl; and z is an integer of 1 up to the valence of H_y and where z is less than the valence of H_y, the remaining valences of H_y are taken up with hydrogens; and H_y is a hydrophilic group selected from

i) morpholino; cyclic mono amide radicals of 5-7 ring members which are selected from carbon and one nitrogen; saturated and unsaturated cyclic radicals having 5-6 ring members of the formula III,



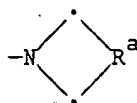
(III)

wherein R^a is alkylene or alkenylene of 2 or 3 carbons, cyclic amides having 6-7 ring members of the formula IV,



(IV)

wherein q and r are each independently 0-2,
and cyclic amines of the formula



(V)

wherein R^a is alkylene or alkenylene of 2 or 3 carbons;

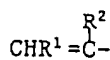
each of which is unsubstituted or substituted by hydroxy -C₁₋₅ alkyl, carboxy, or lower alkyl;

ii) tetrahydrofurfuryl

iii) mono, di and poly saccharide radicals, whether straight chain or cyclic, having up to 12 carbon atoms per saccharide unit, their corresponding sugar alcohol radicals, pentaerythritol radicals, and polyvinyl alcohol radicals; and

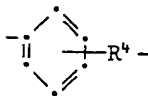
iv) polyhydroxy C₂-C₇ alkyl radicals.

2. The compound of claim 1 wherein X is a group of formula VI

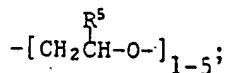


(VI)

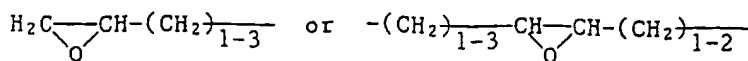
and the portion of div bound thereto terminates in -C(O)R³- of which the carbonyl is bound to X or in



in which the left hand bond is bound to X; wherein either, in case that each of R¹ and R² is hydrogen or methyl, R³ is selected from -O- or -NR⁵-provided that the next atom of div to which it is bound is other than oxygen or nitrogen, or R³ is a bond provided that the next atom of div to which it is bound is other than a carbonyl carbon, and R⁵ is hydrogen or lower alkyl; or in case that R¹ is hydrogen or methyl, and R² is hydrogen, lower alkyl or cyano, R³ is lower alkylene or



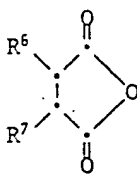
and in each case R⁴ is -O-, -C(O)-, -OC(O)-, -C(O)O-, -NR⁵C(O)-, -OC(O)O-, -NR⁵-, -NR⁵C(O)O-, -C(O)NR⁵-, -OC(O)NR⁵-, or -NR⁵C(O)NR⁵-provided that the next atom of div to which it is attached is other than oxygen or nitrogen; or X is an epoxy group of the formulae



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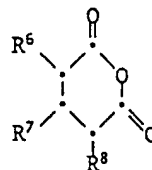
or X is an anhydride residue of the formulae VIII or IX,

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(VIII)

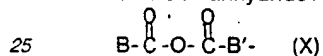
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(IX)

wherein at least one of R^6 and R^7 in formula VIII and at least one of R^6 - R^8 in formula IX is a bond, the others being a bond, hydrogen, lower alkyl or two adjacent groups R^6 - R^8 in formula IX together with the atoms to which they are attached form a C_{5-8} cycloalkyl or cycloalkenyl ring or form a benzene or naphthalene ring; and the unsaturated analogs thereof;

or X is an anhydride residue of the formula X,



wherein B is C_1 - C_6 alkyl, C_2 - C_6 alkenyl or phenyl or naphthyl or has the meaning of B' , and B' is C_1 - C_6 alkylene, C_2 - C_6 alkenylene or phenylene or naphthylene;

or X is isocyanato, isothiocyanato, amino, or -NH(loweralkyl);

or X is an acyl, preferably carboxyl, or is an acyl halide, preferably an acyl chloride, or is an acyl ester, preferably of a lower alkyl alcohol, more preferably of a primary alcohol, or an amide, preferably of a lower alkyl amine, more preferably of a lower alkyl primary amine;

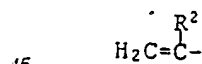
or X is a carbamoyl of the formula XI



wherein R^9 is amino lower alkyl;

or X is an ether group of the formula -O- R^{10} wherein R^{10} is lower alkyl or is a cyclic ether residue having a total of 4 to 7 ring members only one of which is oxygen, the remaining ring members being carbon, the bond to div being other than the alpha and omega carbons of the ring when it is bound to an oxygen atom of div; or X is hydroxy.

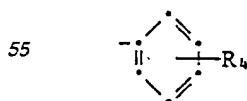
3. The compound of claim 1 wherein X is 1-methylvinyl, 2-methylvinyl, or allyl; or



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wherein R^2 is hydrogen or methyl and the portion of div to which it is attached terminates in -C(O)- R^3 - with the carbonyl being bound to X, and R^3 is -O- or - NR^5 - with R^5 being hydrogen or lower alkyl; or $\text{H}_2\text{C}=\text{CH}$ - and the portion of div to which it is attached terminates in

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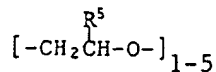
the left hand bond being bound to X, wherein R^4 is -O-, - NR^5 -, -C(O)-, -C(O) NR^5 -, or -C(O)O-; or

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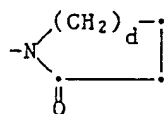
wherein R^2 is hydrogen, lower alkyl, or cyano and the portion of div to which it is attached terminates in $-\text{C}(\text{O})-\text{R}^3$, the carbonyl thereof being bound to X and R^3 being lower alkylene or



and R^5 being lower alkyl.

4. The compound of claim 1 wherein Hy is selected from

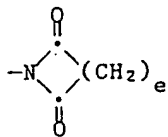
- ba) morpholino which is unsubstituted or mono- up to tetra-substituted by lower alkyl;
- bb) an amide of the formula XII



(XII)

wherein d is 1-3; each of which is unsubstituted or substituted by lower alkyl;

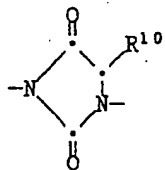
bc) a group of formula XIII,



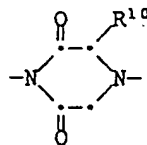
(XIII)

wherein e is 2-3; each of which is unsubstituted or substituted by lower alkyl;

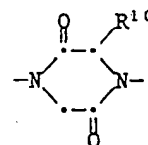
bd) a divalent group of one of the formulae XIV, XV, XVa, XVI, XVIIa or XVIIb,



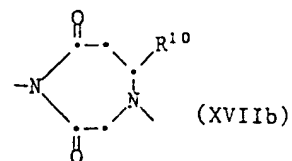
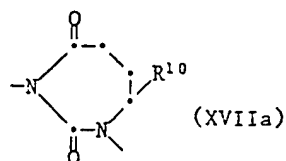
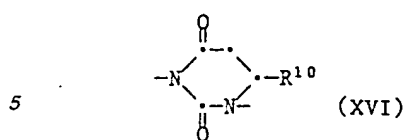
(XIV)



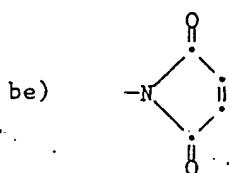
(XV)



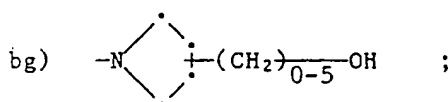
(XVa)



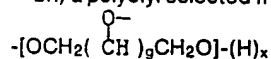
10 wherein R¹⁰ is hydrogen or carboxy;



30 wherein f is one or two, each of which is unsubstituted or substituted by lower alkyl;

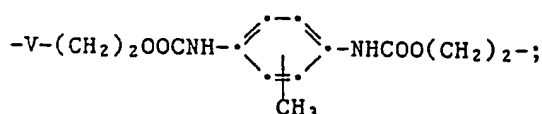


45 bh) a polyolyl selected from bha) polyvinyl alcohol radicals, bhb) groups of the formula



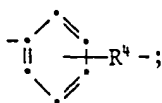
50 wherein g is 2-10 and x is an integer from 0.5 g up to g + 1 inclusive; cyclic saccharide analogs thereof; di-tetra saccharides thereof, preferably having saccharide-saccharide links between the 1 and 4 carbon positions, preferably β links; bhc) $\text{C}(\text{CH}_2\text{O})_4(\text{H})_i$ wherein i is 0-3; and bhd) polyhydroxy lower alkylene, preferably C₂₋₃ alkylene, glycol radicals; wherein in bha) and bhd) above, at least one and up to 50 % of the hydroxy groups are missing their alcoholic hydrogens.

55 5. The compound of claim 1 wherein div is selected from
-V-(CH₂)₂NHCOO(CH₂)₂-;

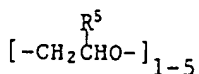


65 -V-(CH₂)₂NHCO-; and

-V-(CH₂)₂NHCO(CH₂)₂- in which V is selected from a bond, -C(O)R³-, or



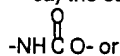
in each case the left hand bond of V being bound to X; and wherein R³ is -O-, -NR⁵- or



or a bond; R⁵ is hydrogen or lower alkyl; and R⁴ is a bond, -O-, -C(O)-, -OC(O)-, -OOC-, -OC(O)O-, -NR⁵-, -NR⁵C(O)-, -C(O)NR⁵-, -NR⁵COO-, -OOCNR⁵-, or -NR⁵C(O)NR⁵-.

6. The compound of claim 1 wherein X is vinyl, 1-lower alkyl vinyl, 2-lower alkyl vinyl, 1,2-di(lower alkyl)vinyl or vinyl-lower alkyl, Hy is pyrrolid-5-one-1-yl, morpholin-1-yl, glycidyl,

(-OCH₂-[CH] ₃₋₆ -CH₂O-)H₄₋₇ radicals, (HOCH₂)₃C-, [HOCH₂]₃C-CH₂O-, or a polyvinylalcohol radical, div is an alkyl of 2-6 carbons which is terminated on one side by carbonyloxy, ca) the carbonyl being bound to X and being interrupted once by



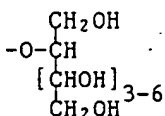
cb) terminated at the other side by



the carbonyl being bound to Hy, preferably the carbonyl being bound to an oxygen atom of Hy; or a divalent -C(O)O-aliphatic-OC(O)NH-aryl-NHC(O)O-aliphatic-group with the terminal carbonyl group being bound to X.

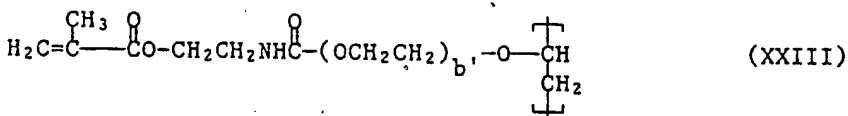
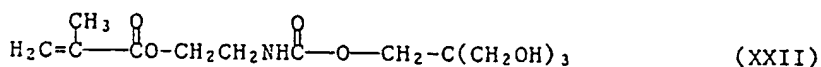
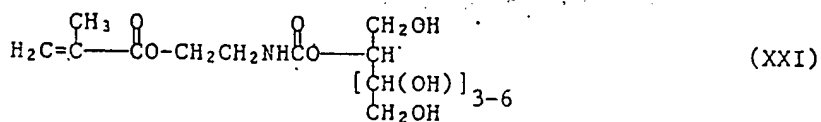
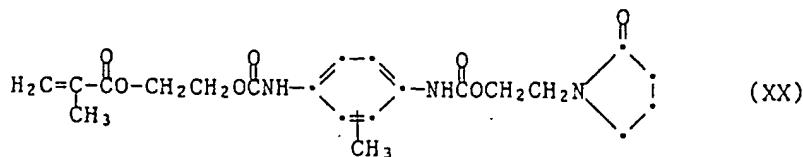
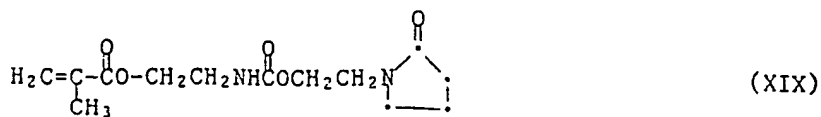
7. The compound of claim 1 wherein X is vinyl or 1-methyl vinyl; z is one; div is selected from -C(O)O-C₂₋₆-alkyl- which is interrupted once by -NHC(O)O- within the the alkyl portion, the terminal carbonyl group being bound to X; the same group as defined directly hereinbefore terminated on the alkyl side by 1 to 19 additional oxyalkylene groups; -C(O)O-C₂₋₆-alkyl-NHCO-, the terminal carbonyl group of the oxycarbonyl portion being bound to X; -aryl-NHCO-, the aryl-portion of which is bound to X; -aryl-NHC(O)O-C₂₋₄-alkyl-, the aryl-portion of which is bound to X; and -C(O)O-C₂₋₆-alkyl- which is interrupted once by -OCONH-aryl-NHCOO- in the alkyl portion, the terminal carbonyl group of which is bound to X; wherein aryl is phenyl or phenyl substituted by C₁₋₄-alkyl, preferably methyl;

and Hy is selected from pyrrolidin-5-one-1-yl, morpholin-1-yl, glycidyl, -C(CH₂OH)₃,

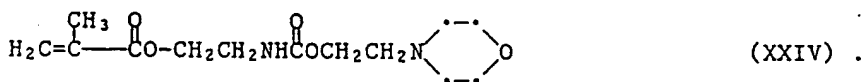


and polyvinylalcohol radicals.

8. The compound of claim 1 which is selected from a compound of formula

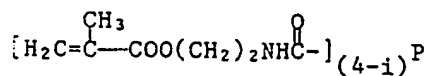


where b' is the number of repeating units in a typical polyethyleneglycol, especially on average 1 to 20, and formula XXIII represents a portion of a modified polyvinylalcohol macromer; and

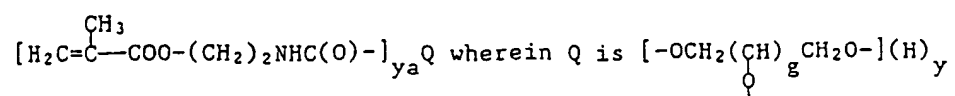


9. The compound of claim 8 wherein said hydrophilic modifying monomer is selected from the compounds of formula XIX, XX and XXIV.

10. The compound of claim 1 which is selected from



wherein P is $\text{C}(\text{CH}_2\text{O})_4\text{H}_i$ and i is 0-3; or p is a polyvinyl alcohol having at least one and up to 50% of the alcoholic hydrogens thereof absent; and



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in which g is 1-6 and y is zero up to g + 1 and y_a is (g + 2 - y).

11. Use of a compound of formula I of claim 1 for the manufacture of a homopolymer or copolymer containing polymerized units of said compound of formula I.

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54 **Hydrophilic modifier monomers.**

57 Hydrophilic modifier monomers of the formula $(X-div)_zHy$ are disclosed wherein X is a reactive group, Hy is a hydrophilic group and div is a divalent linking group, z being a number up to the available valence of Hy, excess Hy valences being taken up by hydrogen. The monomers of the invention can be used to boost the hydrophilic nature of a wide variety of polymeric materials or be polymerized themselves with varying degrees of copolymerizable monomers. They are particularly suited for making hydrophilic contact lens materials.

EP 0 331 633 A3



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EUROPEAN SEARCH REPORT

Application Number

EP 89 81 0121

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 216 074 (CIBA-GEIGY) * Claims 1-40; examples 1,2,23,25 *	1-11	C 08 F 8/00 G 02 B 1/00 C 08 F 20/36
X	US-A-4 670 506 (M. GOLDENBERG) * The whole document *	1-11	
A	EP-A-0 134 861 (TORAY INDUSTRIES) * Claims 1-12 *	1	
A	GB-A-2 182 661 (ARMSTRONG WORLD INDUSTRIES) * Claims 1-21 *	1	
A	EP-A-0 249 306 (AUTOTYPE INTERNATIONAL) * Claims 1-12 *	1	
A	EP-A-0 226 079 (BASF) * Claims 1-9 *	1	
A	US-A-3 928 299 (H.J. ROSENKRANZ) * Claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,X	EP-A-0 276 631 (CIBA-GEIGY) * Claims 1-10; page 5, lines 35-58 *	1-11	C 08 F G 02 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-08-1992	Examiner PERMENTIER W.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid.
- namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions.

namely:

see sheet -B-

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid.
- namely claims:
- ☐ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.
- namely claims:



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EP 89 81 0121 -B-

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims 1a, 2-11 : Ethylenically unsaturated polymerizable compounds.
2. Claims 1b-1m : Reactive compounds.